EVIDENCE FOR EXTREME DEUTERIUM ENRICHMENT IN RADICALS OF THE INSOLUBLE ORGANIC MATTER OF ORGUEIL BY PULSED ELECTRON PARAMAGNETIC RESONANCE O. Delpoux[1], D. Gourier[1], H. Vezin[2], L. Binet[1], S. Derenne[3] and F. Robert[4], [1]CNRS UMR 7574, Laboratoire de Chimie de la Matière Condensée de Paris, Ecole Nationale Supérieure de Chimie de Paris (11 rue Pierre et Marie Curie, F-75231 Paris cedex 05, France, didier-gourier@enscp.fr), [2]CNRS UMR 8009, Laboratoire de chimie organique et macromoléculaire, Université des sciences et technologie de Lille (59655 Villeneuve d'Ascq, France), [3]CNRS UMR 7618, Laboratoire de chimie bioorganique et organique physique, Ecole Nationale Supérieure de Chimie de Paris (11 rue Pierre et Marie Curie, F-75231 Paris cedex 05, France), [4]Laboratoire d'étude de la Matière Extraterrestre, Museum National d'Histoire Naturelle (61 rue Buffon, 75005 Paris, France).

Introduction: Insoluble organic matter (IOM) of carbonaceous chondrites, the most primitive meteorites, may represent an important reservoir of prebiotic molecules that probably contributed to the emergence of life on Earth. Despite its primitive character, this IOM is the result of complex processes and contains relics which survived heating, mixing, chemical reactions and hydrothermal alteration in the parent body and which exhibit very high deuterium enrichments similar to those found in cold interstellar clouds [1]. Using NanoSIMS, deuterium was recently shown to be heterogeneously distributed in IOM as highly D-enriched hot spots were observed [2]. The heterogeneous nature of the organic matter of carbonaceous chondrites (Orgueil, Murchison, Tagish Lake) was also evidenced through Continuous Wave Electron Paramagnetic Resonance (CW-EPR), which showed–that IOM contains high concentrations of molecular moieties containing unpaired electron spins in π molecular orbitals, that are very inhomogeneously distributed. Local radical concentrations reach $\approx$ 4 to 5×10^{19} spins.g^{-1}, compared with bulk average values 1.8×10^{18}, 7×10^{18} and 2×10^{19} spins.g^{-1} for Murchison, Orgueil and Tagish Lake, respectively thus pointing to the occurrence of radical hot spots [3,4]. It is thus tempting to determine if a correlation exists between deuterium hot-spots and radical hot-spots. Unfortunately, the hyperfine interaction (interaction of the electron spin with elements bearing non-zero nuclear spins, i.e ^{1}H, ^{2}H, ^{13}C, ^{14}N, …) is not resolved in the CW-EPR line of IOM [3]. More sophisticated EPR techniques, such as Electron-Nuclear Double Resonance (ENDOR) and pulsed-EPR spectroscopies may provide information on the nature of nuclear spins interacting with the unpaired electron spins. In this preliminary work, we used the Electron Spin Enveloppe Echo Modulation (ESEEM) technique to reveal the presence of a very high concentration of deuterium in the radical moieties of IOM in Orgueil meteorite.

Results and Discussion: Like modern NMR, pulsed EPR proceeds by using sequences of microwave pulses of finite duration to generate spin echos, the intensity of which is monitored as a function of the time delay between specific pulses. When nuclear spins interact with the electron spin, this interaction induces a modulation of the echo amplitude at frequencies corresponding to magnetic nuclear frequencies. We used a four pulses sequence $\pi/2$–τ–$\pi/2$–t_1–π–t_2–$\pi/2$–τ–echo (4P-ESEEM), where τ, t_1 and t_2 are time intervals between microwave pulses, and $\pi/2$ and π represent the angles of rotation of the electron spin magnetization induced by microwave pulses. Figure 1 shows the Fourier transform of the 4P-ESEEM recorded with τ=196 ns as a function of t_1=t_2. This spectrum reveals peaks at nuclear frequency ν_I and combination peaks at $2\nu_I$ of hydrogen (^{1}H), deuterium (^{2}H or D) and carbon ^{13}C nuclei interacting with the unpaired electron spin.

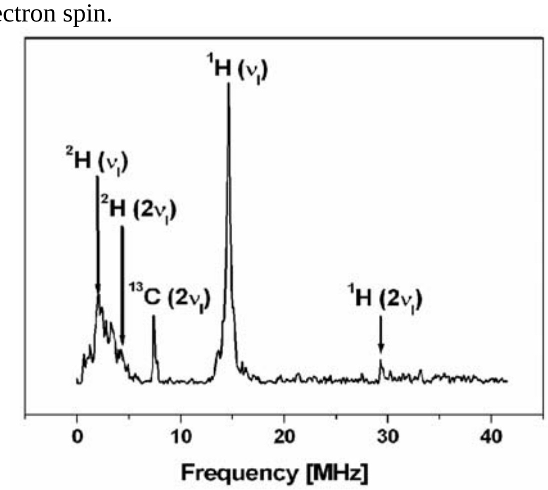

Figure 1: Four- pulse ESEEM spectrum at 10 K of the IOM of Orgueil. τ=196 ns.

It is important to note that deuterium, with a natural abundance on Earth of 0.0148 %, cannot be detected by pulsed EPR if its concentration with respect to normal hydrogen is less than ~1 %. The fact that a relatively strong signal is observed at 2.2 and 4.4 MHz (ν_I and $2\nu_I$ for deuterium), indicates that the ratio D/H in radicals is larger than 1%. However a more accurate value of D/H can be obtained only after a detailed mathematical treatment of the spectrum, which is currently underway. This result indicates that the deuterium-rich hot spots observed by Nanosims [2] also correspond to radical hot spots detected by EPR.

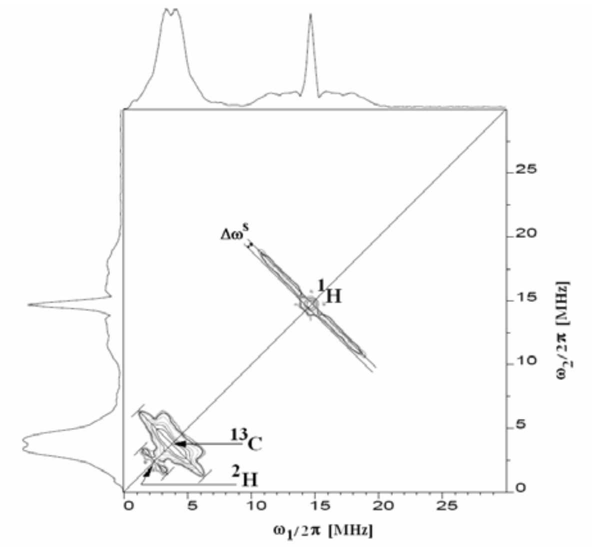

Figure 2: Two-dimensional plot of the 4P-ESEEM spectrum of the IOM of Orgueil.T=10 K; τ=200 ns.

Another interesting feature is revealed by recording 4P-ESEEM spectra as a function of pulse delays t_1 and t_2, and using a two-dimensional representation of the Fourier transform versus the corresponding frequencies $\omega_1/2\pi$ and $\omega_2/2\pi$. Figure 2 shows the contour plot of the intensity of such 2D spectrum for Orgueil at 10 K. Spots along the diagonal $\omega_1/2\pi = \omega_2/2\pi$ occur at nuclear frequencies ν_I of ^{2}H, ^{13}C et ^{1}H nuclei, and represent nuclei weakly interacting with electron spins (i. e. distant nuclei). Correlation peaks outside the diagonal give the frequencies of the electron-nuclear interaction (hyperfine interactions A) with nuclei located in radical moieties. In the simple situation where hydrogen and deuterium are localized on the same types of CH bonds we would expect the following relation between hyperfine interactions of the two isotopes:

$$\mathrm{A}(^1H)/\mathrm{A}(^2H) = g_H / g_D = 6.51$$

where g_H and g_D are the nuclear g-factors of hydrogen and deuterium. Experimentally we found a value 0.46 for this ratio, which indicates that deuterium sites of the radicals are different from hydrogen sites in IOM radicals. This result shows that radicals exhibit highly exchangeable CH bonds and other CH bonds that are not, or weakly exchangeable. This is in agreement with a recent study based on δD values of individual pyrolysis and oxidation products of Orgueil IOM [5]

Conclusion: Pulsed Electron Paramagnetic Resonance has been used to analyze the isotopic composition of radicals in IOM of Orgueil meteorite. It is shown that radicals, which are heterogeneously distributed in the IOM, contain a very high deuterium-concentration (D/H > 1%), much larger than the average bulk value D/H = 0.035 % for this meteorite. This preliminary result indicates that deuterium is mainly located in radical moieties of the IOM of Orgueil, implying that deuterium hot-spots observed by Nanosims correspond to radical hot spots of the IOM. In addition, pulsed EPR shows that these radicals possess highly exchangeable CH bonds together with non-exchangeable (or poorly exchangeable) CH bonds. This result confirms the hypothesis according to which the most exchangeable H host the higher D/H ratio. If correct, such observation has profound implication for the origin of the enrichment in Deuterium of the Solar System. We have qualitatively checked that the same result is obtained for Tagish Lake IOM.

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